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of the autumn and winter months at the beginning and end of the contest year than between the egg production of these months and the productions of the intervening spring and summer months.

The relationship between the intensity of correlation and the degree of separation of the periods of egg production compared is best illustrated by the results for April and the five preceding and the six following months. The magnitude of the constants decreases with fair regularity from March to the preceding November and from May to the following October.

The second law is best exemplified by the coefficients measuring the relationship between November or October production and the record of the other months. Note that in the biological year of this investigation these months do not fall in the same but in different calendar years.

The results are to appear in detail in *Genetics*.<sup>3</sup>

<sup>1</sup> Harris, Blakeslee, Warner, and Kirkpatrick, *Genetics, Cambridge*, 2, 1917, (36-77). Also these PROCEEDINGS, 3, 1917, (237-241).

<sup>2</sup> Harris, *Biometrika, Cambridge*, 6, 1909, (438-443).

<sup>3</sup> A treatment of the relationships between part of the year's yield and the output for the entire year is in preparation by Mr. L. E. Card for a Bulletin of the Storrs Experiment Station.

## TWO LAWS GOVERNING THE IONIZATION OF STRONG ELECTROLYTES IN DILUTE SOLUTIONS AND A NEW RULE FOR DETERMINING EQUIVALENT CONDUCTANCE AT INFINITE DILUTION DERIVED FROM CONDUCTIVITY MEASUREMENTS WITH EXTREMELY DILUTED SOLUTIONS OF POTASSIUM CHLORITE

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Communicated by A. A. Noyes, August 4, 1917

Any theoretical interpretation, in terms of the Ionic Theory, of the properties and behavior of any solution containing electrolytes involves as one of its essential factors a knowledge of the degrees of ionization of the electrolytes present in the solution. The most reliable method of determining the degree of ionization,  $\alpha_C$ , of a uni-univalent electrolyte at the concentration  $C$  is by means of the relationship,  $\alpha_C = \Lambda_0/\Lambda_C$ , where  $\Lambda_C$  is its equivalent conductance (corrected if necessary for viscosity effects) at the concentration  $C$ , and  $\Lambda_0$  is its equivalent conductance at zero concentration.

The value of  $\Lambda_0$  is usually obtained by extrapolating to zero concentration, some empirical function which is found to represent more

or less satisfactorily the observed relation between  $\Lambda$  and  $C$  over at least the lower portions of the concentration range. The lowest concentration to which any observer has hitherto found it practicable to push accurate conductivity measurements is 0.0001 normal. (Measurements by Kohlrausch<sup>1</sup>). This limitation of the concentration range open to measurement is due to the magnitude of the 'water correction' in the very dilute solutions, and to the uncertainty involved in applying it. Conductivity water which is approximately stable in contact with the atmosphere has a specific conductance of the order of magnitude of  $1.10 \times 10^{-6}$  reciprocal ohms, due to the impurities (chiefly  $\text{CO}_2$ ) which it dissolves from the air. The 'water correction' which must therefore be applied to the measured value of the conductivity of a dilute salt solution may amount at 0.0001 normal to as much as 10%, at 0.00001 normal to as much as 100%, and at 0.000001 normal to as much as 1000% of the conductivity of the salt itself. And, aside from the magnitude of the correction the proper method of applying it is rendered uncertain owing to our lack of knowledge of the exact nature and amounts of the impurities present in the conductivity water, as well as to lack of sufficient constancy in the value of the conductivity of the water during the time which is required to prepare and measure the conductivity of the salt solution.

The  $\Lambda_0$  values in use at present have, consequently, been obtained by extrapolation from conductivity data which in the most favorable cases do not extend below 0.0001 normal and which in most cases stop at 0.001 normal. The values of  $\Lambda_0$  selected by different observers using the same conductivity data are, therefore, almost as numerous as the different functions which have been proposed for representing the data over the range open to measurement, ranging, for example, in the case of KCl at 18° from  $\Lambda_0 = 128.3$  (Kraus and Bray<sup>2</sup>), and  $\Lambda_0 = 128.5$  (Wegscheider<sup>3</sup>) to  $\Lambda_0 = 130.0$  (Kohlrausch; Noyes and Falk<sup>4</sup>). Now unless the  $\Lambda_0$  value for a salt can be determined with a certainty of at least 0.01 to 0.02% we cannot hope to obtain any information concerning questions which involve a knowledge of the concentration of the un-ionized molecules of strong electrolytes in dilute solutions, such questions, for example, as the behavior of strong electrolytes with respect to the requirements of the Mass-Action Law.

About eight years ago the writer became convinced that the only possible way of securing an answer to these much discussed questions was to obtain accurate conductivity data in the range of concentrations below 0.0001 normal, and that, in spite of the great difficulties which such an investigation presented, the questions at stake were of

sufficient importance to make the attempt worth while. Accordingly, with the aid of a grant from the Bache Fund of the National Academy, the investigation was begun in 1911.

The first part of the problem consisted in developing and perfecting the Kohlrausch method for measuring the conductance of electrolytes so that an accuracy of better than 0.01% could be obtained in measuring the conductance of very pure water and of these very dilute solutions. With the valued assistance of Dr. J. E. Bell and Mr. Karr Parker this part of the problem was successfully solved, and the results have already been published.<sup>5</sup>

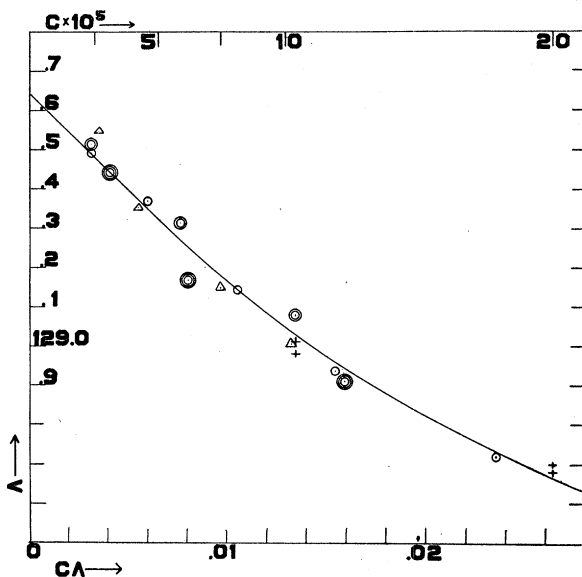


FIG. 1

The second part of the problem resolved itself into the preparation of large quantities of conductivity water which should be practically chemically pure, and the preservation of the purity of this water during the operations of preparing and measuring the conductivity of the solutions. This was successfully accomplished by means of a large quartz still connected to a three-liter quartz conductivity cell provided with platinum electrodes sealed into quartz tubes, the distillation being carried out in a current of carefully purified air. In this way three liters of conductivity water having a specific conductance at 18° of only  $0.05 \times 10^{-6}$  reciprocal ohms could be obtained and preserved in the conductivity cell for at least 12 hours without any appreciable increase in its specific conductance. The solutions were made up by

dropping into this cell small individual crystals of potassium chloride weighed out on an assay balance. In this way the conductivity data were carried down to 0.00002 normal.

The values obtained are shown in figure 1 ( $\Lambda$ ,  $C\Lambda$  curve), which is taken from the thesis of Dr. H. J. Weiland,<sup>6</sup> to whose careful work the final success of the investigation has been largely due. In this figure are represented four independent series of experiments, through which the best representative curve is drawn. The small crosses show the values found by Kohlrausch and Maltby.

In order to determine the value of  $\Lambda_0$ , and also the limiting value,  $K_0$ , of the mass-action expression as the concentration approached zero, it is necessary to extrapolate from 0.00002 normal. Of the various methods which have been employed for extrapolating conductivity data, those of Kohlrausch<sup>1</sup> and of Noyes,<sup>4</sup> as well as all others which are based upon the assumption that the electrolyte does not obey the Mass-Action Law within any concentration range must, it seems to the writer, be rejected because the known behavior of such electrolytes is entirely in harmony with obedience to the Mass-Action Law in sufficiently dilute solutions. Functions of the form

$$\frac{\alpha^2 C}{1 - \alpha} = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)} = K_E = K_0 + k \left( C \frac{\Lambda}{\Lambda_0} \right)^h$$

which have been proposed and employed by Kraus and Bray<sup>2</sup> must also be rejected, because, although in form they reduce to the Mass-Action Law when  $C = 0$ , they cannot as a matter of fact be made to represent the conductivity data in dilute solutions, being nothing more than empirical interpolation equations which will express approximately (0.1%) the variation of conductivity with concentration between 0.001 and 2 normal. The recent function proposed by Bates,<sup>7</sup>  $\log K_E = \log K'_0 + k' \left( C \frac{\Lambda}{\Lambda_0} \right)^{h'}$  expresses very accurately the conductivity data for potassium chloride between 0.0001 normal (the lowest concentration reached by Kohlrausch) and 1 normal, but it also cannot be made to express the conductivity data below 0.0001 normal. Both the Kraus equation and the Bates equation fulfil the condition of obedience to the Mass-Action Law when  $C = 0$ , but they both impose upon the electrolyte an arbitrary method of approach to the condition of constancy required by the Mass-Action Law. The two methods of approach are both radically different and both wrong, since neither form of function can be fitted to the data in the most dilute solutions. In fact, any method of extrapolation which imposes an arbitrary a priori determined path by

which the values of  $K_E$  shall approach constancy must obviously be rejected if we expect to obtain reliable values for  $\Lambda_0$  and  $K_0$ .

In order to avoid the errors involved in what may be called the 'arbitrary function' method of extrapolating, and also in order to avoid the uncertainties involved in attempting a direct graphical extrapolation, the following method was devised. It rests only upon the following two assumptions: (1) That as  $C$  decreases, the value of the mass-action expression  $K_E$  also decreases and gradually approaches a constant,

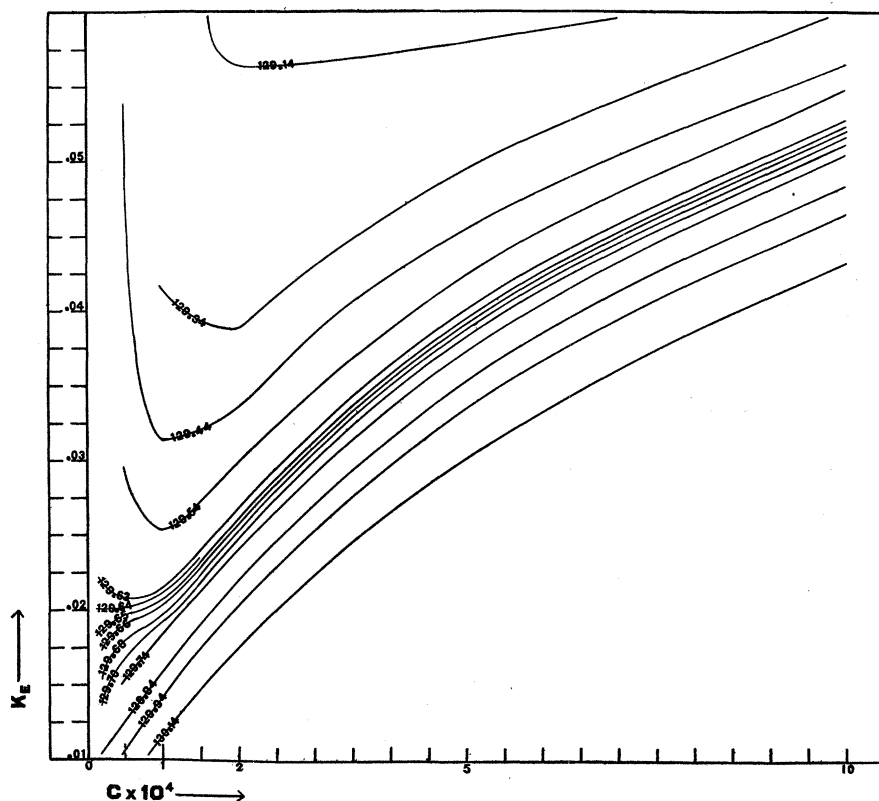


FIG. 2

$K_0$ , at extreme dilutions; and (2) that when the value of  $K_E$  once begins to approach a constant value, it will not thereafter, that is in more dilute solutions, exhibit any erratic behavior such as a rapid rise as the concentration decreases, or a sudden fall under the same conditions. In other words, it is assumed that those influences which cause a strong electrolyte to deviate from the Mass-Action Law gradually and steadily become smaller and smaller and finally disappear at high dilutions.

The method consists simply in plotting values of  $K_{\text{eq}}$ , the mass-action expression, against values of the concentration, employing different assumed values of  $\Lambda_0$  and rejecting such values of  $\Lambda_0$  as cause the curve in dilute solutions to exhibit sudden changes in direction. In this way it is found that, if too small a value is employed for  $\Lambda_0$ , the curve will eventually shoot upward; while, if too large a value is employed, it will turn downward in the lower concentration ranges. By employing this method it is possible to determine the value of  $\Lambda_0$  with a certainty of 0.01%, provided the conductance data themselves are as accurate as this and extend at least as low as 0.00002 normal.

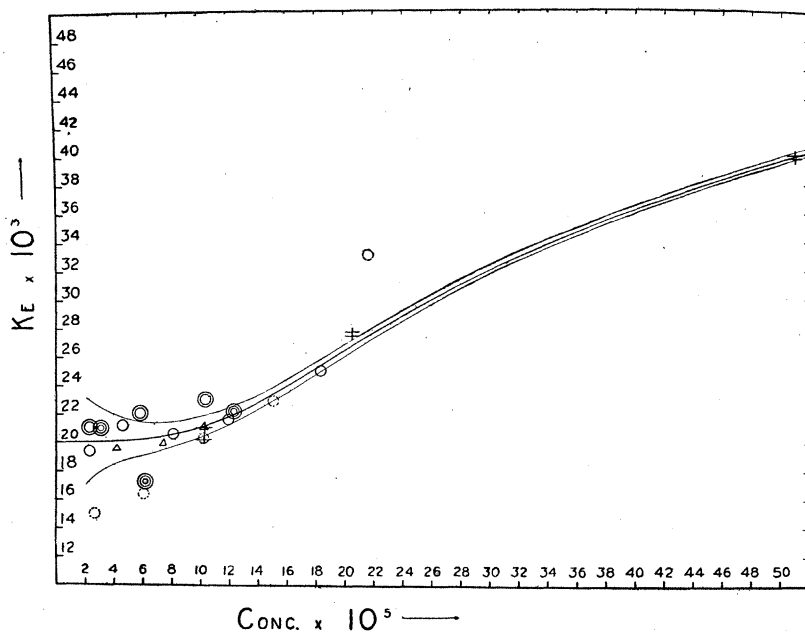


FIG. 3

This will become evident from an examination of figure 2, which has been constructed from conductance values which are substantially those represented by the curve in figure 1. It is also evident from this figure that the value of  $\Lambda_0$  for potassium chloride at  $18^\circ$  is  $129.64 \pm 0.02$ , and that the value of  $K_0$  is  $0.020 \pm 0.001$ .

Figure 3 illustrates the behavior of potassium chloride with respect to the requirements of the Mass-Action Law and shows that this law is obeyed within the experimental error in the concentration range 0 to 0.0006 normal. The different series of points represent independent sets of measurements. Those indicated by the dotted circles represent

a rejected series. The two bounding curves above and below the heavy curve represent the shift in the position of this 'best' curve which would be produced by a total error of 0.02%; for instance, an error of 0.01% in the concentration in combination with an error of 0.005° in the temperature of the solution. Since most of the observed points fall within the limits set by these two curves, it is evident that the agreement among them is even better than could be expected, considering all of the difficulties and chances of error involved in the work. A detailed account of Dr. Weiland's work will be published later.

With the aid of the conductivity data for potassium chloride presented above, it becomes possible to establish two general laws with respect to the behavior of strong electrolytes in dilute solutions. These laws may be stated as follows:

1. In sufficiently dilute solution (i.e., for all practical purposes below 0.0001 normal) all uni-univalent salts of strong acids and bases obey the Mass-Action Law, and all of them have the same ionization constant.

2. In sufficiently dilute solutions the values of the mass-action expression for all such salts are identical, the identity persisting up to higher concentrations the more nearly the salts under comparison resemble each other, and in any case persisting within the experimental error up to 0.0002 normal for all salts which have been accurately measured at these concentrations. In the case of two salts, such as potassium chloride and potassium bromide, for example, which resemble each other very closely, this identity persists up as high as 0.005 normal.

With the aid of the second of these laws it is now possible to derive a general rule by means of which the  $\Lambda_0$  value for any uni-univalent salt can be accurately obtained from the value of the equivalent conductance of that salt at a single concentration, say 0.0001 normal. This rule is deduced as follows:

The second law stated above is expressed mathematically by the equation,

$$\frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)} = K_E$$

where the value for  $K_E$  is independent of the nature of the salt, and can therefore be read off from the curve in figure 3 (or preferably from a similar curve for a salt resembling as closely as possible the one under examination). Solving this expression we find (with sufficient accuracy),  $\Lambda_0 = \Lambda_C \left(1 + \frac{C}{K_E}\right)$ , an expression by means

of which the value of  $\Lambda_0$  for any salt can be calculated from a single value of  $\Lambda_C$  for that salt. A convenient value of  $C$  to employ generally for this purpose is 0.0001, and for this concentration the above expression becomes  $\Lambda_0 = 1.00476 \Lambda_{0.0001}$  for all uni-univalent salts of strong acids and bases.

The reason why strong acids and bases themselves, as well as salts of weak acids and bases, are not included in the scope of the laws as formulated above, is not because there is any reason to suppose that these substances form exceptions to the laws, but merely because there are no reliable data available for testing the laws in any of these cases, nor can such data be secured except by employing extremely pure water, such as that described above.

The new rule for calculating  $\Lambda_0$  has been tested at concentrations 0.0001 and 0.0002 in the case of all salts for which there are reliable data available, and in every instance the rule applied to both concentrations is found to give within the experimental error the same  $\Lambda_0$  value. As an illustration of this, the data for a few of the salts whose conductivities are most accurately known are shown in the accompanying table. A general revision of  $\Lambda_0$  values and ionic conductances on the basis of the above laws will be published later.

TABLE

ILLUSTRATING THE CALCULATION OF  $\Lambda_0$  VALUES FOR TYPICAL UNI-UNIVALENT SALTS BY MEANS OF THE GENERAL RELATION,  $\Lambda_0 = \Lambda_C \left(1 + \frac{C}{K_E}\right)$ , AND DEMONSTRATING THE IDENTITY OF THE  $K_E$  VALUES OF ALL SUCH SALTS UP TO  $C = 0.0002$ . [MEASUREMENTS BY KOHLRAUSCH AND MALTBY,<sup>1</sup> CORRECTED (+ 0.02%) FOR METATHESIS BUT NOT FOR ATOMIC WEIGHTS.]

$C \times 10^4$ EQUIVALENTS PER LITER	NaCl		KNO <sub>3</sub>		LiCl		LiNO <sub>3</sub>	
	$\Lambda_C$	$\Lambda_0$	$\Lambda_C$	$\Lambda_0$	$\Lambda_C$	$\Lambda_0$	$\Lambda_C$	$\Lambda_0$
1.037	108.20	108.72	125.48	126.09	98.17	98.63	94.48	94.92
	108.11	108.63	125.54	126.15	98.11	98.57	94.44	94.88
	108.04	108.57						
$K_E = 0.0212$	Mean	108.64 $\pm$ .05	Mean	126.12 $\pm$ .03	Mean	98.60 $\pm$ .03	Mean	94.90 $\pm$ .02
2.053	107.83	108.65	125.16	126.11	97.85	98.58	94.16	94.90
	107.82	108.64	125.22	126.17	97.86	98.59	94.14	94.88
	107.82	108.64						
$K_E = 0.0268$	Mean	108.64 $\pm$ .01	Mean	126.14 $\pm$ .03	Mean	98.59 $\pm$ .01	Mean	94.89 $\pm$ .01
0.5212								
$K_E = 0.02017$	108.41	108.69						

- <sup>1</sup> Friedrich Kohlrausch, *Gesammelte Abhandlungen*, Leipzig, 1911.  
<sup>2</sup> Kraus, C. A., and Bray, W. C., *J. Amer. Chem. Soc., Easton, Pa.*, **35**, 1913, (1412).  
<sup>3</sup> Wegscheider, *Zs. physik. Chem., Leipzig*, **69**, 1909, (603).  
<sup>4</sup> Noyes, A. A., and Falk, K. G., *J. Amer. Chem. Soc., Easton, Pa.*, **34**, 1912, (461).  
<sup>5</sup> Washburn, E. W., and Bell, J. E., *Ibid.*, **35**, 1913, (177); Washburn, *Ibid.* **38**, 1916, (2431); Washburn and Parker, K., *Ibid* **39**, 1917, (235).  
<sup>6</sup> Weiland, H. J., *Urbana, Univ. Ill. Theses*, 1917.  
<sup>7</sup> Bates, S. J., personal communication to the writer. See Washburn's *Introduction to the Principles of Physical Chemistry*, New York, 1915, p. 216. Bates does not propose his function as a basis for selecting the value of  $\Delta_0$ . For this purpose he employs a method which, while based upon substantially the same character of assumptions as the one adopted by the writer and giving nearly the same results, does not seem so direct and simple in its application. See Bates, *J. Amer. Chem. Soc., Easton, Pa.*, **35**, 1913, (526).

## ON THE GROWTH AND FECUNDITY OF ALCOHOLIZED RATS

By E. C. MacDowell and E. M. Vicari

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Communicated by C. B. Davenport, August 16, 1917

In the course of an experiment conducted primarily for a different purpose, we have obtained data upon the effect of large doses of inhaled alcohol on the growth and fecundity of a series of albino rats. From the time of weaning (28 days) the alcohol was administered daily. Except for the first few weeks when the doses were lighter, the rats were left in the inhalation tanks till they could no longer stand upon their feet and could move but very feebly, if at all. The purpose was to give as heavy a dose as possible without killing the animal. This took different times for different rats, and the time required on different days varied according to the intensity of the alcohol vapor in the tanks. No data were recorded as to the time required to regain normal activity, but it may be said in general that this was roughly a matter of three to four hours.

For each rat alcoholized, a normal control from the same litter and of the same sex was raised. These controls were kept in companion cages adjacent to their corresponding alcoholic sibs. Except for the alcohol treatment, all the rats were given the same care and attention.

Weekly weighings were made of all the rats and individual growth curves were plotted. From these curves the weights at the ages given in the standard growth curves of Donaldson were estimated. In making these estimations, allowances were made for temporary losses in weight due to food conditions or minor illnesses; in doing this the whole curve of the individual was considered as well as the curves of its sibs and the standard Wistar curves. The weights so obtained were averaged for the two groups of rats, and these averages plotted in figure 1.